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(56) Documents cited
GB A 2152525 **GB 0674896**
GB A 2151657 **EP A1 0091237**
GB A 2015561 **EP A1 0003172**
GB 1540386 **US 2580713**

(58) Field of search
C5D
Selected US specifications from IPC sub-class C11D

(54) Detergent gel compositions

(57) Stable aqueous detergent gels wholly or predominantly in hexagonal liquid crystal form contain a principal non-ethoxylated non-soap anionic surfactant in which the head group is positioned terminally or next-to-terminally on a hydrocarbon chain, for example, a primary alkyl sulphate or an alpha-olefin sulphonate, together with either an auxiliary surfactant or a specified additive.

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SPECIFICATION

Detergent compositions

- 5 *Technical field* 5
- The present invention relates to detergent compositions in the form of a stable transparent, translucent or opaque water-soluble gel which is wholly or predominantly in hexagonal liquid crystal form. The compositions of the invention are especially suitable for washing dishes or other hard surfaces, but are also of use for other cleaning purposes, for example, fabric washing.
- 10 *Background and prior art* 10
- US 2 580 713 (Wood/Procter & Gamble) describes paste or gel detergent compositions which are in hexagonal or "middle" phase. These compositions contain certain anionic detergents, notably triethanolamine lauryl sulphate, generally in admixture with water-soluble soaps. Use of alkanolamine as the principal cation
- 15 facilitates middle phase formation. 15
- GB 2 155 031A (Unilever), published on 18 September 1985, describes and claims detergent compositions in hexagonal phase gel form. The principal ingredient of these gels is a "secondary" surfactant, that is to say, its polar head group is positioned non-terminally in a hydrocarbon chain or carries two or more hydrocarbon chains. Examples of "secondary" surfactants are alkylbenzene sulphonates and dialkyl sulphosuccinates. These
- 20 surfactants will not form hexagonal phase spontaneously at ambient temperature, and the gels contain an "additive", for example, urea or sodium xylene sulphonate, that forces the composition into hexagonal phase. A simple gel of this type may contain alkylbenzene sulphonate, urea and water. 20
- Turkish Patent No. 21612 (Mintax), laid open to public inspection on 5 December 1984, also discloses detergent gels containing alkylbenzene sulphonate, urea and water, but contains no reference to hexagonal
- 25 phase. 25
- The "secondary" surfactants to which the aforementioned GB 2 155 031A (Unilever) relates will tend to form lamellar phase rather than hexagonal phase, and need an "additive" such as urea to stabilise the hexagonal phase. "Primary" surfactants such as alkyl sulphates, in which the head group is positioned terminally or next to terminally on a hydrocarbon chain, are subject to a different problem: they tend to crystallise. A urea-type
- 30 "additive" does not overcome this difficulty. According to US 2 580 713 mentioned above this problem is solved by using alkanolamine as the principal cation. 30
- We have now discovered that it is possible to extend substantially the range of concentrations over which hexagonal phase gels stable at 22°C can be prepared from "primary" non-ethoxylated non-soap surfactants, even in sodium salt form, by the inclusion in the gels of a second component which may either be an auxiliary
- 35 surfactant of a defined type or a specific type of non-surfactant "additive". 35
- Definition of the invention*
- The present invention accordingly provides an aqueous detergent composition comprising a gel wholly or predominantly in hexagonal liquid crystal form, wherein the gel comprises:
- 40 (a) from 5 to 85% by weight of a non-ethoxylated micelle-forming non-soap surfactant having an anionic head group and an aliphatic or araliphatic hydrocarbon chain containing from 10 to 20 aliphatic carbon atoms, the anionic head group being positioned terminally or next to terminally in the hydrocarbon chain, and 40
- (b) a second component comprising
- (b) (i) from 1 to 75% by weight of an auxiliary micelle-forming non-soap surfactant selected from:
- 45 (b) (i) (i) anionic non-soap surfactants other than those defined under (a) above, ethoxylated nonionic surfactants having HLB values of at least 12, and amine oxides; or 45
- (b) (i) (ii) fatty acid mono- and diethanolamides, and ethoxylated nonionic surfactants having HLB values lower than 12;
- and /or
- 50 (b) (ii) 1 to 15% by weight of an additive which is a non-micelle-forming or weakly micelle-forming aliphatic, alicyclic, aromatic or araliphatic nonionic material having a melting point not exceeding 55°C and a dielectric constant of at least 2.2, selected from: 50
- (b) (ii) (i) materials containing at least 4 carbon atoms, and containing a hydroxyl group positioned terminally or within 2 carbon atoms of the terminal position on a hydrocarbon chain or on an aromatic or alicyclic ring, and optionally one or more further polar groups; containing not more than 6 aliphatic carbon atoms if the
- 55 hydroxyl group is the only polar group present or if a second polar group is present and separated from the hydroxyl group by 2 or less carbon atoms; or containing not more than 12 aliphatic carbon atoms if a second polar group is present and separated from the hydroxyl group by 3 or more carbon atoms; or 55
- (b) (ii) (ii) materials containing at least 7 carbon atoms, and containing at least one polar group positioned terminally or within 2 carbon atoms of the terminal position on a hydrocarbon chain or on an aromatic or
- 60 alicyclic ring, and/or containing ethylenic unsaturation; 60
- the total amount of (a) plus (b) being within the range of from 15 to 95% by weight; and, optionally,
- (c) from 1 to 45% by weight of a second additive which is an anionic or nonionic water-soluble non-micelle-
- 65 forming or weakly micelle-forming material having a polar head group and optionally an aliphatic or 65

araliphatic hydrocarbon chain containing at most 6 aliphatic carbon atoms;
component (c) being essential if neither an auxiliary surfactant (b)(i)(i) nor an additive (b)(ii)(i) is present; and
(d) water.

5 *Disclosure of the invention*

The detergent gels of the invention are characterised by being wholly or predominantly in hexagonal liquid crystal form. This crystal form, also known as "middle" phase, may be recognised by various microscopic techniques, of which X-ray diffraction is the most definitive: hexagonal phase compositions give rise to a characteristic X-ray diffraction pattern unique to this liquid crystal form. The ratio between the Bragg spacings in the X-ray pattern is

$$1 : \frac{1}{\sqrt{3}} : \frac{1}{\sqrt{4}} : \frac{1}{\sqrt{7}}$$

see, for example, "Liquid Crystals and Plastic Crystals", edited by G W Gray and P A Winsor (Ellis Horwood Ltd, 1974), volume 2, chapter 4, page 88.

Of the three liquid crystal forms – lamellar, hexagonal and cubic – hexagonal phase is intermediate in rigidity, but rigidity or viscosity is not an infallible means of distinguishing hexagonal phase gels from other gels because, for example, softer lamellar phase gels can be thickened with polymer or electrolytes to produce products of comparable viscosity. The products of the invention are inherently stiff gels, and require no thickening agent. Preferred embodiments are transparent or translucent, and are sufficiently attractive in appearance for packaging in transparent containers.

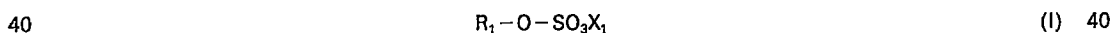
The detergent gels of the invention comprise the following ingredients:

- (a) the principal surfactant,
- (b) the second component which is
 - (b) (i) the auxiliary surfactant, and/or
 - (b) (ii) the additive,
 - (c) the optional second additive,
- (d) water.

These are described in more detail below. In addition, certain other ingredients conventionally used in detergent products may be present, also as described below.

The principal surfactant (a)

- The principal surfactant (a) may be any non-ethoxylated non-soap anionic surfactant in which the anionic headgroup is positioned on the terminal or next-to-terminal carbon atom of a hydrocarbon chain containing from 10 to 20 aliphatic carbon atoms. Examples of such surfactants include the following:
 - (i) Primary alkyl sulphates of the general formula I



wherein R_1 is an alkyl group having from 10 to 20 carbon atoms and X_1 is a solubilising cation. Primary alkyl sulphates may be substantially of a single chain length, as in dodecyl sulphate; or they may consist of mixtures of materials of different chain length, as in coconut alkyl sulphate ($C_{10} - C_{14}$, with C_{12} and C_{14} predominating).

- (ii) Alpha-olefin sulphonates of the general formula II



wherein R_2 is an alpha, beta-unsaturated $C_{10} - C_{20}$ alkenyl group and X_2 is a solubilising cation.

- (iii) Primary alkane sulphonates of the general formula III



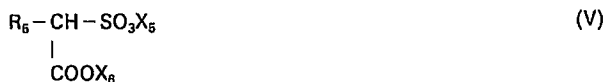
wherein R_3 is an primary $C_{10} - C_{20}$ alkyl group and X_3 is a solubilising cation.

- (iv) Alkyl or alkenyl isethionates of the general formula IV



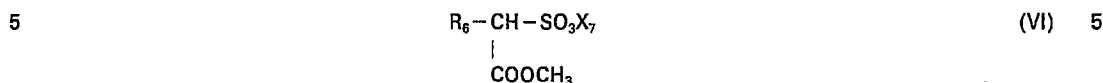
where R_4 is a $C_7 - C_{20}$ alkyl or alkenyl group and X_4 is a solubilising cation.

- (v) Alpha-sulphonated fatty acid salts (SFAS) of the general formula V



wherein R_5 is a $C_8 - C_{20}$ alkyl group, X_5 is a solubilising cation, and X_6 is H or a solubilising cation (the same as or different from X_5), depending on pH.

(vi) Fatty acid methyl ester sulphonates (FAES) of the general formula VI



wherein R_6 is a $C_8 - C_{20}$ alkyl group and X_7 is a solubilising cation. Fatty acid methyl ester sulphonates may be substantially of a single chain length, or may consist of mixtures of materials of different chain length, as in coconut FAES ($C_8 - C_{18}$, with R_6 as C_{10} and C_{12} predominating). 10

It will be seen that all these preferred surfactants contain a sulphonate or sulphate head group in a terminal or next-to-terminal position, and in some cases this is modified by the presence of a nearby carboxyl or carboxylic ester group.

15 The counteraction of the principal surfactant component (a) may be any solubilising cation, provided that the Krafft point of the surfactant or surfactant/additive system as a whole is below ambient temperature. Examples include alkali metal, such as sodium, potassium, lithium or caesium; alkaline earth metal, such as magnesium; ammonium; substituted ammonium, such as mono-, di- or trialkylamine or mono-, di- or trialkanolamine. 15

Trialkanolamine salts have the advantage that because the molecular weight of the cation is high the water content of a given composition will be reduced, as compared with a similar sodium salt composition, and the concentration of surfactant and (if present) additive will be increased: in practice this increases the range of compositions over which robust commercial gels can be prepared. Sodium salts, on the other hand, are easy to prepare by neutralisation with caustic soda. The choice of cation is therefore very much a matter of preference. 20

The principal surfactant component (a) of the compositions of the invention may be constituted by any one or more of the materials listed above. 25

In one preferred embodiment of the invention, the principal surfactant (a) comprises or consists of one or more primary alkyl sulphates.

Proportions of ingredients present

30 In the compositions of the invention, the principal surfactant (a) is present in an amount of from 5 to 85% by weight, preferably from 5 to 75% and more preferably from 8 to 55% by weight, the most preferred level depending on whether an auxiliary surfactant (b)(i) or an "additive" (b)(ii), or both, is or are present. The preferred level also depends on the counteraction of the principal surfactant, and will be larger if the cation is of high molecular weight, for example, triethanolamine, than if it is of low molecular weight, for example, sodium. 30

35 For sodium salts, the preferred level is from 5 to 60% by weight, more preferably from 5 to 55% by weight. 35

The total amount of components (a) and (b) present, whether (b) is an auxiliary surfactant or an additive or both, ranges from 15 to 95% by weight, preferably from 15 to 85% by weight. Again the preferred amount depends on the counteraction of the principal surfactant, and, if an anionic auxiliary surfactant is present, on its counteraction too. In an all-sodium system the total level of (a) plus (b) is preferably within the range of from 30 to 60% by weight. The water content is preferably from 15 to 85% by weight in general, and preferably from 40 to 70% by weight in an all-sodium system. As detailed below, the most preferred ranges within these ranges will differ according to whether component (b) is an auxiliary surfactant (i) or an additive (ii), or a mixture of the two. 40

The total surfactant level, that is to say, the total level of the principal surfactant (a) plus any auxiliary surfactant (b)(i) present, is preferably within the range of from 15 to 80% by weight. The lower end of this range - 15 to 60% by weight - is especially applicable to all-sodium systems, while total surfactant levels of 60 to 80% will normally be attainable only if the cation of one or both surfactants is of high molecular weight, for example, triethanolamine. The region of hexagonal phase formation will of course vary with the principal surfactant, the auxiliary surfactant (if present) and the proportions in which the two are present: these variations will be illustrated in the Examples at the end of this specification. 45 50

The auxiliary surfactant (b)(i)

In a first embodiment of the invention, the compositions of the invention contain an auxiliary non-soap surfactant (b)(i) selected from specified anionic and nonionic surfactants.

55 In this first embodiment, the compositions of the invention contain from 1 to 75% by weight, preferably from 5 to 50% by weight, more preferably from 8 to 40% by weight, of the auxiliary surfactant (b)(i), and also preferably contain from 5 to 60% by weight, more preferably from 5 to 40% by weight, of the principal surfactant (a). Again, the preferred levels depend on the counteraction of the principal surfactant, and on that of the auxiliary surfactant if the latter is anionic. The term "principal surfactant" is not intended to carry the implication that this component necessarily predominates, and indeed the ratio of (a) to (b)(i) can range from 20:1 to 0.1:1, preferably from 10:1 to 0.1:1, the preference depending on the particular auxiliary surfactant chosen. 60

The total active detergent level in this embodiment preferably ranges from 16 to 60% by weight, in an all-sodium system. It is of course possible for more than one of each surfactant from each of the categories (a) and (b)(i) to be present.

65 Two subgroups of auxiliary surfactant suitable for use in the present invention have been recognised. The first, 65

(b)(i)(i), consists of anionic non-soap surfactants other than those of the same type as the principal surfactant (a), that is to say, anionic non-soap surfactants other than non-ethoxylated anionic surfactants in which the anionic headgroup is positioned terminally or next-to-terminally on the C₁₀ to C₂₀ hydrocarbon chain; ethoxylated nonionic surfactants having high (≥ 12.0) HLB values; and amine oxides. Preferred classes of

5 (b)(i)(i) auxiliary surfactants are:

(1) non-ethoxylated anionic surfactants in which the anionic headgroup is positioned non-terminally in an aliphatic or araliphatic hydrocarbon chain;

(2) ethoxylated anionic surfactants;

(3) ethoxylated nonionic surfactants having HLB values ≥ 12.0 ; and

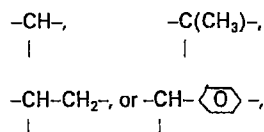
10 (4) amine oxides.

The first group of non-ethoxylated surfactants have been disclosed as ingredients of hexagonal phase gels in the aforementioned GB 2 155 031A (Unilever), where they are referred to as "secondary" surfactants.

In a "secondary" anionic surfactant, the anionic head group is either attached to the hydrophobic hydrocarbon chain in a non-terminal position, or itself occupies a non-terminal position within the chain, that is to say, two or
15 more shorter chains are directly attached to the head group itself. The first type of "secondary" surfactant will generally conform to the general formula VII



wherein Z is the anionic head group, for example, a sulphonate or sulphate group in combination with a solubilising cation; R₇ and R₈ are aliphatic or araliphatic hydrocarbon chains together containing from 8 to 20 carbon atoms, the shorter of R₇ and R₈ containing at least 2 aliphatic carbon atoms; and Y is a linking group such as



the total number of aliphatic carbon atoms in R₇, R₈ and Y being at least 8, preferably 10 to 28.

Examples of this first type of "secondary" anionic surfactant include alkylbenzene sulphonates, secondary alkane sulphonates and secondary alkyl sulphates. All these materials are generally random mixtures of isomers,
35 and will include some material that is not "secondary", that is to say, with a terminally or next-to-terminally positioned head group, but the average constitution of the material will be "secondary".

The second type of "secondary" anionic surfactant will generally conform to the general formula VIII



wherein Z is the anionic head group, in combination with a solubilising cation, and R₉ and R₁₀ are aliphatic or araliphatic hydrocarbon chains together containing at least 8, preferably 10 to 28, aliphatic carbon atoms, the
45 shorter of the chains R₉ and R₁₀ containing at least 2 aliphatic carbon atoms.

Examples of this second type of "secondary" anionic surfactant are dialkyl sulphosuccinates.

For the purposes of the present invention, preferred "secondary" non-ethoxylated anionic surfactants are the linear or branched alkylbenzene sulphonates containing an average of from 8 to 15, preferably 10 to 13, aliphatic carbon atoms.

50 Alkylbenzene sulphonates may advantageously be combined with the principal surfactant (a) at weight ratios of (a) to (b)(i) of from 10:1 to 0.25:1. If the principal surfactant (a) is one or more primary alkyl sulphates, the preferred ratio range is from 5:1 to 0.67:1, more preferably from 4:1 to 1:1.

Preferred ethoxylated anionic surfactants for use in the compositions of the invention are the alkyl ether sulphates. These are materials of the general formula IX



wherein R₁₁ is an alkyl group containing from 10 to 20, preferably from 12 to 15, carbon atoms; X₈ is a solubilising cation; and n, the average degree of ethoxylation, ranges from 1 to 12, preferably from 1 to 8.

60 As with the principal surfactant (a), the choice of solubilising cation for the anionic auxiliary surfactant (b)(i)(i) is very much a matter of preference.

Preferred high-HLB ethoxylated nonionic surfactants are the ethoxylated alcohols and alkyl phenols, which are materials of the general formula X



wherein x is zero (alcohol ethoxylates) or 1 (alkylphenol ethoxylates); R_{12} is an alkyl group having from 6 to 20 carbon atoms; and m , the average degree of ethoxylation, ranges from 5 to 30. For alcohol ethoxylates, R_{12} preferably has from 8 to 18 carbon atoms, and m is from 5 to 14. Examples of suitable alcohol ethoxylates include Dobanol (Trade Mark) 91-8 and 91-6 ex Shell (C_9 - C_{11} alcohol; $m=8$ and 6 respectively; HLB values 13.8 and 12.6 respectively). For alkylphenol ethoxylates, R_{12} preferably has from 8 to 12 carbon atoms and m is from 6 to 16.

Ethoxylated auxiliary surfactants, both anionic and nonionic, may advantageously be combined with the principal surfactant (a) at weight ratios of (a) to (b)(i) of from 10:1 to 0.1:1. If the principal surfactant (a) is one or more primary alkyl sulphates, the preferred ratio range is from 5:1 to 0.1:1, more preferably from 3.5:1 to 0.14:1.

The amine oxides are materials of the general formula XI



wherein R_{13} is a C_{10} - C_{20} alkyl group, R_{14} is a C_1 - C_4 alkyl group, and R_{15} is a C_1 - C_4 alkyl group.

Amine oxides may advantageously be combined with the principal surfactant (a) at weight ratios of (a) to (b)(i) of from 20:1 to 2:1. If the principal surfactant is one or more primary alkyl sulphates, the preferred ratio range is from 10:1 to 3:1, more preferably from 7:1 to 3:1.

The second class of auxiliary surfactants (b)(i)(ii) consists of ethoxylated nonionic surfactants of low (<12.0) HLB value, and fatty acid mono- and diethanolamides.

Preferred ethoxylated nonionic surfactants are the ethoxylated alcohols and alkyl phenols of the general formula X given above, but generally with lower degrees of ethoxylation m than the higher-HLB materials; an example is Dobanol (Trade Mark) 91-5 ex Shell (C_9 - C_{11} alcohol; $m=5$; HLB 11.7). These may advantageously be combined with the principal surfactant (a) at weight ratios of (a) to (b)(i) of from 10:1 to 0.1:1. If the principal surfactant (a) is one or more primary alkyl sulphates, the preferred ratio range is from 5:1 to 0.1:1, more preferably from 3.5:1 to 0.14:1.

The fatty acid mono- and diethanolamides are materials of the general formula XII



wherein R_{16} is an alkyl group containing from 7 to 20 carbon atoms, and R_{17} is H or $-CH_2CH_2OH$.

Fatty acid mono- and diethanolamides may advantageously be combined with the principal surfactant (a) at weight ratios of (a) to (b)(i) of from 20:1 to 2:1. If the principal surfactant is one or more primary alkyl sulphates, the preferred ratio range is from 10:1 to 3:1, more preferably from 7:1 to 3:1.

The significance of the distinction between the two broad classes of auxiliary surfactant (b)(i)(i) and (b)(i)(ii) is that the optional second additive (c), which will be discussed in more detail below, is required when the auxiliary surfactant is of the (b)(i)(ii) type. When the auxiliary surfactant is of the (b)(i)(i) type, the second additive (c) may if desired be present, but it is not essential.

If desired, the compositions of the invention may contain mixtures of auxiliary surfactants, of the same type or of different types.

50 The additive (b)(ii)

In a second embodiment of the invention, the compositions contain in addition to the principal surfactant (a) an "additive" (b)(ii) which is not a surfactant. The additive (b)(ii) is a non-micelle, forming or weakly micelle-forming aliphatic, alicyclic aromatic or araliphatic nonionic material having a melting point not exceeding 55°C, and a dielectric constant of at least 2.2. The additive (b)(ii) has the ability to lower the Krafft temperature of the surfactant system below ambient temperature. As with the auxiliary surfactants (b)(i), the additives (b)(ii) fall into two broad classes (b)(ii)(i) and (b)(ii)(ii), the optional second additive (c) being essential only when the additive (b)(ii) is of the (b)(ii)(ii) type, and optional or advantageous when the additive (b)(ii) is of the (b)(ii)(i) type.

The first class of additives, (b)(ii)(i), is composed of materials that are additionally capable of extending the range of compositions in which hexagonal phase exists and is stable. These are relatively short-chain organic materials containing a hydroxyl group, which may be alcoholic or phenolic. If desired one or more additional polar groups may be present in the molecule, for example, a further hydroxyl group or a carboxyl, carboxylic acid ester, carboxylic acid amide, amine, aldehyde, or ketone group. The (b)(ii)(i) additive should contain at least 4 carbon atoms, the maximum number of carbon atoms that may be present being governed by the number and disposition of any polar groups present other than the hydroxyl group. If no other polar group is present, or if a

second polar group is present but separated from the hydroxyl group by 2 or less carbon atoms, the (b)(ii)(i) additive should contain not more than 6 aliphatic carbon atoms; while if a second polar group separated from the hydroxyl group by 3 or more carbon atoms is present, the (b)(ii)(i) additive should contain not more than 12 aliphatic carbon atoms. These limitations are imposed by the necessity for the (b)(ii)(i) additive to have some, but not too much, affinity for water.

Examples of suitable (b)(ii)(i) additives, with melting points and dielectric constants (above the melting point), include the following:

		<i>Melting point</i>	<i>Dielectric constant</i>	
10				10
	2-phenylethanol	<20°C	11.5	
	hydroxycitronellal	<20°C	11-12	
	benzyl alcohol	<20°C	13.1	
15	thymol	51°C	about 9	15

The second class of additives (b)(ii)(ii) is composed of materials that are not in themselves capable of extending the hexagonal phase region but which solve the problem of crystallisation by lowering the Krafft temperature of the surfactant or surfactant mixture present, while taking the composition into lamellar phase rather than hexagonal phase. As previously mentioned, when the additive (b)(ii) is of this type, it is essential that a second type of additive (c), as defined in the aforementioned GB 2 155 031A (Unilever), also be present in order to force the composition into hexagonal phase. The additives (c) are discussed in more detail below.

The additives (b)(ii)(ii) are poorly water-soluble amphiphilic materials of which the overall character is hydrophobic despite the presence of polar groups. They contain at least 7 carbon atoms, and may contain a polar group positioned terminally or within 2 carbon atoms of the terminal position on a hydrocarbon chain or on an aromatic or alicyclic ring, and/or may contain ethylenic unsaturation. The dielectric constant of the (b)(ii)(ii) additive is at least 2.2. The polar group, if present, may be, for example, a hydroxyl, carboxyl, carboxylic acid ester, carboxylic acid amide, amine, aldehyde, or ketone group.

Examples of such materials, with melting points and dielectric constants (above the melting point), include the following:

		<i>Melting point</i>	<i>Dielectric constant</i>	
35	decan-1-ol	7°C	about 7	35
	dodecan-1-ol	26°C	about 5	
	coconut alcohol	40-45°C	4-5	
	oleyl alcohol	6-7°C	about 4	
	decanoic acid	31.5°C	about 2.4	
40	dodecanoic acid	44°C	about 2.4	40
	oleic acid	16.3°C	2.4	
	coconut fatty acid	40-45°C	about 2.4	

Perfume-like ingredients may also be used as (b)(ii)(ii) additives. Examples of such materials, with melting points and dielectric constants (above the melting point), include the following:

		<i>Melting point</i>	<i>Dielectric constant</i>	
50	d-limonene	<20°C	2.3	50
	linalool	<20°C	about 3	
	terpineol	<20°C	about 3	
	amyl cinnamic aldehyde	<20°C	about 12	
	diethyl phthalate	<20°C	about 8	
55	anisole	<20°C	4.3	55

Commercial perfume blends may also be used. Perfume-like ingredients are typically used at a 1 to 5% by weight level with 30 to 60% by weight of the principal surfactant (a).

With both classes of additive (b)(ii)(i) and (b)(ii)(ii), a melting point of 55°C or below is essential, in order to avoid crystallisation of the additive.

Relatively low levels (1-15% by weight, preferably 2-10% by weight) of additive (b)(ii), whether of the (b)(ii)(i) type or of the (b)(ii)(ii) type, are sufficient. The preferred amount of surfactant (a) present in this embodiment will of course depend on its counteraction, and for an all-sodium system will range from 25 to 60% by weight, more preferably from 30 to 50% by weight. The total level of surfactant plus additive in this embodiment preferably ranges from 16 to 60% by weight, more preferably from 35 to 57% by weight, for an all-sodium system. The ratio of

surfactant to additive may range, for example, from 30:1 to 3:1. For a (b)(ii)(i) additive and a primary alkyl sulphate, a preferred ratio range is from 27.5:1 to 3.5:1.

If desired, compositions of the invention may contain both an auxiliary surfactant (b)(i) and an additive (b)(ii).

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The optional additive (c)

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The compositions of the invention may also contain a second type of additive (c), and indeed this is essential when component (b) is an auxiliary surfactant of the (b)(i)(ii) type, or an additive of the (b)(ii)(ii) type that is not of itself a hexagonal phase promoter. The second additive (c) is also useful in other embodiments to counteract the effect of electrolyte which tends to diminish the size of the hexagonal phase region, and is thus especially advantageous in compositions containing electrolytic components such as builders.

The additive (c) is described in detail in the aforementioned GB 2 155 031A (Unilever). It is a water-soluble non-micelle-forming or weakly micelle-forming material capable of driving the surfactant mixture or surfactant/additive mixture from lamellar phase into hexagonal phase, or of increasing the region of stable hexagonal phase available with a particular composition. The mechanism of action of the additive (c) is not clearly understood; it is possible that it acts so as to increase micelle or liquid crystal curvature, but the scope of the invention is not to be limited by this hypothesis. Empirically it has been observed that some materials useful as hydrotropes in light-duty liquid detergent compositions may behave as type (c) additives. These are generally molecules containing a large polar group and, optionally, a small hydrophobic group, such as an aliphatic or araliphatic chain containing not more than 6, preferably 4 or less, aliphatic carbon atoms. The larger the polar head group, the larger the hydrophobe that can be tolerated.

The polar group of the additive (c) may carry an ionic charge, but if so this must be of the same polarity as that of the surfactant or surfactants, that is to say, anionic. Examples of anionic additives (c) are the lower aryl or alkylaryl sulphonates, such as toluene and xylene sulphonates.

Alternatively the additive (c) may be a highly polar but uncharged material. A preferred type of uncharged additive (c) is typified by the lower amides, containing the -CON- group. Common features of this second type appear to be an ability to raise the dielectric constant of water combined with a structure-breaking effect on water. The preferred material, which is both cheap and environmentally unobjectionable, is urea. Short-chain urea homologues and analogues, for example, methyl and ethyl ureas, thiourea, formamide and acetamide, are possible alternatives, but these are of less interest than urea itself in view of various drawbacks such as cost, toxicity or simply a lesser effectiveness as an additive.

If the additive (c) is urea, a buffering agent is advantageously present in order to minimise hydrolysis, especially alkaline hydrolysis, of the urea. A suitable buffer is boric acid, preferably used in an amount of less than 3% by weight, more preferably from 1 to 2% by weight. Buffering may instead be achieved by including triethanolamine as a counteraction in the surfactant system. The buffering capability and greater electrolyte tolerance of triethanolamine as counteraction, compared with say, sodium, allow higher levels of electrolytic components, for example, sodium tripolyphosphate builder, to be incorporated in the compositions of the invention.

The additive (c) is advantageously present at a level of from 1 to 45% by weight, preferably from 5 to 35% by weight. The more additive (b)(ii)(ii) present, and the more electrolyte present, the more additive (c) will be required.

The water (d)

In all embodiments of the invention, water is an essential constituent. The relative proportions of any particular system of surfactant (a), component (b) (auxiliary surfactant or additive), optional second additive (c) and water that will give stable hexagonal phase or predominantly hexagonal phase gels can be ascertained by experiment, and a phase diagram constructed. Samples at various ratios are prepared by mixing, and the phases present can be recognised without difficulty by visual appearance, gross flow properties, appearance in polarised light, and texture observed in a polarising microscope.

Optional additional ingredients

Unbuilt compositions of the invention may consist substantially wholly of surfactant (a), component (b), optional additive (c), and water, plus the usual minor ingredients such as colour, perfume, germicides and preservatives. Such unbuilt compositions are useful for light-duty applications, for example, for dishwashing, as shampoos, or for fabric washing in soft water areas.

Also within the scope of the invention are heavy-duty fabric washing compositions containing ingredients such as builders, fluorescers, bleaches, photobleaches, enzymes, antiredeposition agents, deoperfumes and germicides. Water-soluble organic or inorganic builders, for example, phosphates, citrates or nitrilotriacetates may be incorporated in the composition for the invention but care must be taken that the electrolyte level does not rise to such an extent that the hexagonal phase gel is destabilised. As previously mentioned, the amount of electrolytic builder that can be tolerated can be increased by also including an additive (c), preferably urea. The same considerations apply to other electrolytic ingredients, for example, sodium sulphite bleach.

Alternatively, water-insoluble inorganic builders such as zeolite may be suspended in the gels of the invention. Equally, other useful insoluble materials such as abrasives or peroxyacid bleaches may be present as suspended solids. An especially preferred bleach material is 1,12-diperoxydodecanedioic acid, as described in EP 160 342A (Unilever).

EXAMPLES

The following non-limiting Examples, in which percentages and ratios are by weight, illustrate the invention.

5 *Comparative examples A to D* 5

Attempts were made, by mixing, to prepare hexagonal phase gels containing coconut alkyl sulphate and water. The alkyl sulphate (sodium salt) was Emal (Trade Mark) 10 ex Kao Soap Ltd. The compositions prepared, and their physical states at ambient temperature, in this case 22°C, are shown in the following Table: it will be seen that no stable hexagonal phase gels could be made.

	Alkyl sulphate	Water	Description of product	
A	30	70	Crystals plus solution	
15 B	35	65	Crystals plus solution	15
C	45	55	Mass of crystals	
D	50	50	Mass of crystals	

Examples 1 to 30

20 These Examples illustrate the first embodiment of the invention, in which an auxiliary surfactant (b)(i) is present. 20

Examples 1 to 5

Compositions containing the coconut alkyl sulphate used in Comparative Examples A to D, alkyl ether sulphate and water were prepared by mixing. The alkyl ether sulphate was Synperonic (Trade Mark) 3-S-70S (C₁₃₋₁₅, 3EO, sodium salt) ex ICI. The compositions were as shown in the relevant Table, in which numbers are used to signify 25 compositions (stable gels) according to the invention, and letters are used to signify comparative compositions outside the invention. The alkyl sulphate is shown as (a) and the alkyl ether sulphate as (b)(i). 25

Examples 6 to 12

30 Compositions containing the sodium coconut alkyl sulphate used in previous Examples, together with ethoxylated nonionic surfactant and water, were prepared by mixing. The nonionic surfactant was Dobanol (Trade Mark) 91-8 ex Shell (C₉-C₁₁, 8EO), which has an HLB value of 13.8. The compositions are shown in the relevant Table, in which (b)(i) denotes the nonionic surfactant. In this Table, the expression "two phases" denotes separation into two liquid crystal (hexagonal and lamellar) phases. 35

Examples 13 to 15

Compositions similar to those of Examples 6 to 12 were prepared using as the auxiliary surfactant (b)(i) an ethoxylated alcohol having a lower average degree of ethoxylation, Dobanol 91-6 ex Shell (C₉-C₁₁, 6 EO); this has an HLB value of 12.6. The compositions are shown in the relevant Table. 40

Examples 16 and 17

Compositions containing an even lower ethoxylate, Dobanol 91-5 ex Shell (C₉-C₁₁, 5 EO), HLB value 11.7, were prepared as shown in the relevant Table. The gel of Comparative Example W contained some hexagonal phase but exhibited flow properties. No wholly hexagonal phase gel could be prepared from these ingredients in the absence 45 of a component (c). 45

Attempts to prepare gels using Dobanol 91-2.5 ex Shell (C₉-C₁₁, 2.5 EO, HLB 8.2) without urea were unsuccessful: no hexagonal phase region existed at 22°C in the absence of a component (c).

Example 18

50 Compositions containing sodium coconut alkyl sulphate with a non-ethoxylated nonionic surfactant, coconut diethanolamide (Ethylan (Trade Mark) LD ex Lankro), were prepared as shown in the relevant Table. The gel of Comparative Example AA contained some hexagonal phase but exhibited flow properties. 50

Examples 19 to 22

55 Compositions containing primary alkyl sulphates in sodium salt form (dodecyl in Example 22, coconut in all the others) together with coconut dimethyl amine oxide (Empigen (Trade Mark) OB ex Albright and Wilson) were prepared as shown in the relevant Table. The sodium dodecyl sulphate was a pure laboratory reagent ex British Drug Houses Ltd. 55

60 *Examples 23 to 26* 60

Compositions containing sodium coconut alkyl sulphate with a linear C₁₀-C₁₂ alkylbenzene sulphonate, Marlon (Trade Mark) A ex Hüls, were prepared as shown in the relevant Table.

Examples 27 and 28

65 Compositions containing ethoxylated nonionic surfactant as the auxiliary surfactant (b)(i), and sodium 65

tripolyphosphate builder, were prepared as shown in the relevant Table. The base formulation, of 20% sodium dodecyl sulphate and 20% Dobanol 91-8, was similar to Example 9 above. Without urea (Comparative Examples KK and LL) an unstable hexagonal phase could be obtained which melted at around ambient temperatures. With 10% urea, hexagonal phase gels stable both at 50°C and at ambient temperature were obtained.

- 5 Comparative experiments without the auxiliary surfactant, using 40% sodium dodecyl sulphate, gave solid crystals (Comparative Examples PP to SS). 5

Example 29

- A stable hexagonal phase gel containing the triethanolamine salt of coconut alkyl sulphate (80%), Dobanol 91-8 (5%) and water (15%) was prepared. The (a): (b)(i) ratio was 16:1. The very high total active detergent level will be noted: because of the high molecular weight of the triethanolamine cation the region for stable hexagonal gel formation occurs at higher active detergent levels than is the case for the sodium salt. 10

Examples 30 to 33

- 15 Compositions containing sodium alpha-olefin sulphonates (AOS) of various chain lengths as the principal surfactant (a) were prepared as shown in the relevant Table. The C₁₄ and C₁₄₋₁₈ materials were ex Lion Corporation, Japan and the C_{14/16} AOS was ex Aekyung Shell, Korea. The auxiliary surfactants used were Dobanol 91-8 and Dobanol 91-5, and, as expected, urea was required in order to obtain a stable gel with the latter (lower HLB) material. In each case the total active detergent level was 50% by weight and the ratio of (a) (b)(i) was 4:1. 20

Examples 34 to 38

- Stable hexagonal phase gels were prepared, as shown in the relevant Table, containing various primary non-ethoxylated anionic surfactants (a) in conjunction with the nonionic surfactant Dobanol 91-8 as the auxiliary surfactant (b)(i). 25

Examples 39 to 71

These Examples illustrate the second embodiment of the invention, in which an additive (b)(ii) is present.

Examples 39 to 41

- 30 Compositions containing sodium coconut alkyl sulphate as the surfactant and 2-phenylethanol as an additive (b)(ii)(i) were prepared by mixing, the compositions being shown in the relevant Table. 30

Examples 42 to 47

- 35 Compositions containing sodium coconut alkyl sulphate, and hydroxycitronellal

$$(\text{CH}_3)_2 \text{C}(\text{OH})-(\text{CH}_2)_3-\text{CH}(\text{CH}_3)-\text{CH}_2\text{CHO}$$
as an additive (b)(ii)(i) were prepared by mixing, the compositions being shown in the relevant Table. 35

- 40 Examples 48 to 52
Compositions containing sodium coconut alkyl sulphate, and benzyl alcohol as an additive (b)(ii)(i), were prepared by mixing, the compositions being shown in the relevant Table. 40

Examples 53 to 57

- 45 Compositions containing a single-chain-length alkyl sulphate, sodium dodecyl sulphate, and 2-phenylethanol as an additive (b)(ii)(i), were prepared by mixing, the compositions being shown in the relevant Table. 45

Example 58

- A stable hexagonal phase gel prepared by mixing contained 35% sodium coconut alkyl sulphate, 5% thymol (2-isopropyl-5-methylphenol) as an additive (b)(ii)(i) and 60% water. 50

Examples 59 and 60

- 55 Compositions containing sodium coconut alkyl sulphate (35% by weight), and linalool (5% by weight) as an additive (b)(ii)(ii), were prepared with and without urea as an additive (c), as shown below. 55

	Example	Urea (%)	water (%)	Product	
	SSS	—	60	Flowable composition	
	59	10	50	Predominantly hexagonal gel	
60	60	20	40	Predominantly hexagonal gel	60

Example 61

- 65 Compositions containing sodium coconut alkyl sulphate (40% by weight), and a commercial perfume (IFF 114 ex International Flavours & Fragrances Inc, 5% by weight) were prepared with and without urea as an additive (c), as shown below. 65

	Example	Urea (%)	water (%)	Product	
	TTT	—	55	Solution plus lamellar phase	
	61	10	45	Predominantly hexagonal gel	
5	<i>Examples 62 to 64</i>				5
	Compositions containing sodium coconut alkyl sulphate, and terpineol as a perfume-like additive (b)(ii)(ii), were prepared with and without urea as an additive (c), as shown in the relevant Table.				
10	<i>Example 65</i>				10
	Compositions containing sodium coconut alkyl sulphate, and coconut fatty acid as an additive (b)(ii)(ii), were prepared with and without urea as an additive (c), as shown in the relevant Table. It will be seen that with this type of (b)(ii)(ii) additive the further additive (c) is essential to gel formation, but its level must be carefully chosen.				
15	<i>Example 66</i>				15
	The procedure of Example 65 was repeated using decan-1-ol as the additive (b)(ii)(ii), as shown in the relevant Table. Similar results were obtained, a higher level of urea being required for stable gel formation than in Example 65.				
	<i>Examples 67 to 69</i>				
20	Compositions were prepared containing sodium alpha-olefin sulphonate (AOS) as (principal) surfactant (a), together with benzyl alcohol or limonene additive (b)(ii)(i) or (b)(ii)(ii) respectively, as shown in the relevant Table. In each case the total active detergent level was 40% by weight and the ratio of surfactant to additive was 8:1. With limonene, urea was required in order to obtain a stable gel.				20
25	<i>Example 70</i>				25
	A stable hexagonal phase gel was prepared containing sodium coconut fatty acid methyl ester sulphonate (55% by weight), benzyl alcohol (5% by weight) and water. The total active detergent level was 55% by weight, and the ratio of surfactant to additive was 11:1.				
30	<i>Comparative examples JJJJ to LLLL</i>				30
	To show the importance of the chain length and melting point limitations in the definition of the additive (b)(ii), compositions were prepared containing sodium coconut alkyl sulphate (40% by weight) and 5% by weight each of two "additives" that do not meet these requirements: ethanol (only 2 carbon atoms) and stearyl alcohol (melting point 57°C). The results were as follows:				
35					35
	Example	"Additive"	Urea (%)	Product	
	JJJJ	Ethanol	—	Solution plus a few crystals	
	KKKK	Stearyl alcohol	—	Solid	
40	LLLL	Stearyl alcohol	10	Solid	40
	<i>Examples 71 to 79</i>				
	Stable gels in accordance with the invention, suitable for use in washing fabrics, were prepared by mixing. The compositions are shown in the relevant Table. The base gel for Examples 71 to 74 was that of Example 2, and				
45	the base gel for Examples 75 to 79 was that of Example 31.				45
	The fabric washing ingredients incorporated were as follows:				
	Antiredeposition agent: sodium carboxymethyl cellulose, ex Courtaulds (62% active matter)				
50	Germicide: formalin (37%)				50
	Proteolytic enzyme: alcalase solution ex Novo, activity 1600 glycine units/mg.				
	Fluorescer: Tinopal (Trade Mark) CBS-X ex Ciba-Geigy, which is 4,4'-di(2-sulphostyryl)-diphenyl, disodium salt.				
55	Photobleach: aluminium phthalocyanine sulphonate ex Ciba Geigy.				55
	Deoperfume: ex PPF International				
60	Solid peroxyacid bleach: 1,12-diperoxydodecanedioic acid (DPDDA) (12% available oxygen, produced from DPDDA granules ex Degussa slurried in water and filtered to remove water-soluble inorganic salts).				60
	Buffer (to maintain good peroxyacid bleach stability in storage): Citric acid.				
65	All those compositions were stable translucent hexagonal phase gels.				65

Examples 80 to 82

These Examples relate to fabric washing compositions in accordance with the invention containing electrolytic components: sodium tripolyphosphate as a builder, and sodium sulphite as a mild bleaching agent as described in GB 1 417 870 (Unilever) and British Patent Application No. 86 06145 (Unilever). The compositions are 5 shown in the relevant Table: all were stable translucent hexagonal phase gels.

Dishwashing test

The dishwashing performances of three gels according to the invention were evaluated using a standardised test procedure in which soiled plates were washed to a foam collapse end point. Each plate was pre-soiled with 10 5g of a standard cooking oil/starch/fatty acid emulsion in water, and the washing solution in each case consisted of 5g of product dissolved in 5 litres of water (4° French hardness) at 45°C, that is to say, a whole product concentration of 1 g/litre. The gels tested were those of Examples 13 and 30, and a gel (Composition 83) similar to that of Example 23 but containing a different alkylbenzene sulphonate, Dobane (Trade Mark) 102 ex Shell (sodium salt). The results were as shown in the final Table.

EXAMPLES 1 TO 5

Example	(a)	(b) (i)	Water	Total active detergent	Ratio (a):(b) (i)	Product
20						
E	35	5	60	40	7:1	Crystals + solution
F	35	20	45	55	1.75:1	Gel + crystals
1	30	10	60	40	3:1	Stable gel
25						
G	25	5	70	30	5:1	Liquid solution
H	25	10	65	35	2.5:1	Gel + solution
2	25	15	60	40	1.67:1	Stable gel
3	20	20	60	40	1:1	Stable gel
4	10	30	60	40	0.33:1	Stable gel
30						
5	15	30	55	45	0.5:1	Stable gel

EXAMPLES 6 TO 12

Example	(a)	(b) (i)	Water	Total active detergent	Ratio (a):(b) (i)	Product
35						
J	40	5	55	45	8:1	Crystals
6	35	10	55	45	3.5:1	Stable gel
40						
K	30	30	40	60	1:1	Two phases
7	30	10	60	40	3:1	Stable gel
L	30	5	65	35	6:1	Gel + solution
8	20	30	50	50	0.67:1	Stable gel
9	20	20	60	40	1:1	Stable gel
45						
10	15	20	65	35	0.75:1	Stable gel
11	10	30	60	40	0.33:1	Stable gel
M	10	20	70	30	0.5:1	Gel + solution
12	5	35	60	40	0.14:1	Stable gel

EXAMPLES 13 TO 15

Example	(a)	(b) (i)	Water	Total active detergent	Ratio (a):(b) (i)	Product
55						
N	40	10	50	50	4:1	Two phases
P	35	20	45	55	1.75:1	Two phases
Q	35	5	60	40	7:1	Two phases
13	30	10	60	40	3:1	Stable gel
60						
R	20	30	50	50	0.67:1	Liquid solution
14	20	20	60	40	1:1	Stable gel
S	20	10	70	30	2:1	Gel + solution
15	10	30	60	40	0.33:1	Stable gel
T	10	20	70	30	0.5:1	Liquid solution
65						

EXAMPLE 16 & 17

<i>Example</i>	<i>(a)</i>	<i>(b) (i)</i>	<i>Urea</i>	<i>Water</i>	<i>Total active detergent</i>	<i>Ratio (a):(b) (i)</i>	<i>Product</i>	
5								5
U	30	20	—	50	50	1.5/1	Lamellar phase (flows)	
16	30	20	20	30	50	1.5:1	Stable gel	
V	30	15	—	55	45	2:1	Solution plus lamellar phase	
17	30	15	20	35	45	2:1	Stable gel	
10	W	30	10	60	40	3:1	Flowing gel	10
X	20	20	—	60	40	1:1	Solution plus lamellar phase	

EXAMPLE 18

15									15
	<i>Example</i>	<i>(a)</i>	<i>(b) (i)</i>	<i>Urea</i>	<i>Water</i>	<i>Total active detergent</i>	<i>Ratio (a):(b) (i)</i>	<i>Product</i>	
20	Y	35	15	—	50	50	2.33:1	Solution plus lamellar phase	20
	18	35	15	20	30	50	2.33:1	Stable gel	
	Z	30	20	—	50	50	1:5:1	Lamellar phase + solution	
	AA	30	10	—	60	40	3:1	Slightly flowing gel	
	BB	25	10	—	65	35	2.5:1	Liquid solution	
	CC	20	25	—	55	45	0.8:1	Solution + lamellar phase	
25									25

EXAMPLES 19 TO 22

<i>Example</i>	<i>(a)</i>	<i>(b) (i)</i>	<i>Water</i>	<i>Total active detergent</i>	<i>Ratio (a):(b) (i)</i>	<i>Product</i>		
30							30	
DD	45	5	50	50	9:1	Gel + crystals		
19	40	10	50	50	4:1	Stable gel		
EE	35	10	55	45	3.5:1	Two phases		
35	20	35	5	60	40	7:1	Stable gel	35
FF	30	10	60	40	3:1	Two phases		
21	30	5	65	35	6:1	Stable gel		
GG	25	10	65	35	2.5:1	Two phases		
HH	20	20	60	40	1:1	Lamellar phase		
40	JJ	20	15	65	35	1.33:1	Two phases	40
22	8	8	84	16	1:1	Stable gel		

EXAMPLES 23 TO 26

45								45
	Example	(a)	(b) (i)	Water	Total active detergent	Ratio (a):(b) (i)	Product	
50	KK	45	20	35	65	2.25:1	Crystals	50
	LL	45	5	50	50	9:1	Crystals	
	23	40	20	40	60	2:1	Stable gel	
	24	40	10	50	50	4:1	Stable gel	
	26	35	20	45	55	1.75:1	Stable gel	
55	26	30	30	40	60	1:1	Stable gel	55
	MM	20	40	40	60	0.5:1	Two phases	
	NN	20	20	60	40	1:1	Gel + solution	

60

60

65

65

EXAMPLES 27 AND 28

<i>Example</i>	<i>(a)</i>	<i>(b) (i)</i>	<i>STP</i>	<i>Urea</i>	<i>Water</i>	<i>Product (ambient)</i>		
5	MM	20	20	5	—	55	Crystals + liquid	5
	NN	20	20	10	—	50	Crystals + liquid	
	27	20	20	5	10	45	Stable gel	
	28	20	20	10	10	40	Stable gel, a few crystals of STP	
	PP	40	—	5	10	45	Crystals	
10	QQ	40	—	5	20	35	Crystals	10
	RR	40	—	10	10	40	Crystals	
	SS	40	—	10	20	30	Crystals	

EXAMPLES 30 TO 33

Example		Principal surfactant	(a)	Auxiliary surfactant	(b) (i)	Urea	Water	Product (ambient)	
20	30	C ₁₄ AOS	40	91-8	10	—	50	Stable gel	20
	31	C _{14/16} AOS	40	91-8	10	—	50	Stable gel	
	32	C ₁₄₋₁₈ AOS	40	91-8	10	—	50	Stable gel	
	TT	C ₁₄ AOS	40	91-5	10	—	50	Flowing gel	
	33	C ₁₄ AOS	40	91-5	10	10	40	Stable gel	
25									25

EXAMPLES 34 TO 38

<i>Example</i>	<i>Principal surfactant</i>	<i>(a)</i>	<i>(b) (i)</i>	<i>Water</i>	<i>Total active detergent</i>	<i>Product</i>	
30							30
	34	Na coconut isethionate	10	30	60	40	Stable gel
	35	Na decane sulphonate	20	40	40	60	Stable gel
	36	Monosodium alpha-sulpho-dodecanoic acid salt	10	30	60	40	Stable gel
35							35
	37	Sodium/ammonium coconut alpha-sulpho fatty acid salt	10	40	50	50	Stable gel
40	38	Na coconut alpha-sulpho fatty acid methyl ester salt	55	10	35	65	Stable gel
							40

EXAMPLES 39 TO 41

<i>Example</i>	<i>(a)</i>	<i>(b) (ii)</i>	<i>Water</i>	<i>Total detergent plus additive</i>	<i>Ratio (a):(b) (ii)</i>	<i>Product</i>		
50							50	
	UU	50	10	40	60	5:1	Crystals	
	VV	50	7	43	57	7:1	Lamellar phase	
	WW	50	5	45	55	10:1	Crystals	
	XX	45	10	45	55	4.5:1	Lamellar phase	
55	39	45	5	50	50	9:1	Stable gel	55
	YY	45	2	53	47	22.5:1	Crystals	
	40	40	5	55	45	8:1	Stable gel	
	ZZ	40	2	58	42	20:1	Crystals	
	41	35	10	55	45	3.5:1	Stable gel	
60	AAA	35	5	60	40	7:1	Gel + solution	60
	BBB	30	10	60	40	3:1	Gel + solution	

EXAMPLES 42 TO 47

<i>Example</i>	<i>(a)</i>	<i>(b) (ii)</i>	<i>Water</i>	<i>Total detergent plus additive</i>	<i>Ratio (a):(b) (ii)</i>	<i>Product</i>	
5							5
CCC	50	2	48	52	25:1	Crystals	
42	45	10	45	55	4.5:1	Stable gel	
43	45	5	50	50	9:1	Stable gel	
10 44	40	10	50	50	4:1	Stable gel	10
45	40	5	55	45	8:1	Stable gel	
46	40	2	58	42	20:1	Stable gel	
47	35	10	55	45	3.5:1	Gel + a little solution	
15 DDD	35	2	63	37	17.5:1	Gel + solution	15
EEE	25	10	65	35	2.5:1	Solution	

EXAMPLES 48 TO 52

<i>Example</i>	<i>(a)</i>	<i>(b) (ii)</i>	<i>Water</i>	<i>Total detergent plus additive</i>	<i>Ratio (a):(b) (ii)</i>	<i>Product</i>	
20							20
25 FFF	50	10	40	60	5:1	Lamellar phase	25
GGG	50	5	45	55	10:1	Crystals	
48	45	10	45	55	4.5:1	Stable gel	
49	45	5	50	50	9:1	Stable gel	
HHH	45	2	53	47	22.5:1	Crystals	
30 50	40	10	50	50	4:1	Stable gel	30
51	40	5	55	45	8:1	Stable gel	
52	35	10	55	45	3.5:1	Stable gel	
JJJ	35	5	60	40	7:1	Gel + solution	
KKK	35	2	63	37	17.5:1	Gel + solution	
35 LLL	30	10	60	40	3:1	Gel + solution	35

EXAMPLES 53 TO 57

<i>Example</i>	<i>(a)</i>	<i>(b) (ii)</i>	<i>Water</i>	<i>Total detergent plus additive</i>	<i>Ratio (a):(b) (ii)</i>	<i>Product</i>	
40							40
MMM	50	10	40	60	5:1	Lamellar phase	
45 53	50	5	45	55	10:1	Stable gel	45
NNN	50	2	48	52	25:1	Crystals	
54	40	5	55	45	8:1	Stable gel	
55	40	2	58	42	20:1	Stable gel	
56	30	10	60	40	3:1	Stable gel	
50 57	30	5	65	35	6:1	Stable gel	50
PPP	30	2	68	32	15:1	Solution	
QQQ	25	10	65	35	2.5:1	Solution	
RRR	25	5	70	30	5:1	Solution	

55

EXAMPLES 62 TO 64

<i>Example</i>	<i>(a)</i>	<i>(b) (ii)</i>	<i>Urea</i>	<i>Water</i>	<i>Product (ambient)</i>	
60 UUU	40	5	—	55	Two phases	60
62	40	5	10	45	Stable gel	
63	40	5	20	35	Stable gel	
VVV	40	10	—	50	Two phases (liquid)	
WWW	40	10	10	40	Two phases (liquid)	
65 64	40	10	20	30	Stable gel	65

EXAMPLE 65

<i>Example</i>	<i>(a)</i>	<i>(b) (ii)</i>	<i>Urea</i>	<i>Water</i>	<i>Product (ambient)</i>	
5 XXX	40	5	—	55	Solid plus solution	5
65	40	5	10	45	Stable gel	
YYY	40	5	20	35	Mass of crystals	
ZZZ	40	10	—	50	Solid plus solution	
AAAA	40	10	10	40	Two phases (liquid)	
10 BBBB	40	10	20	30	Mass of crystals	10

EXAMPLE 66

<i>Example</i>	<i>(a)</i>	<i>(b) (ii)</i>	<i>Urea</i>	<i>Water</i>	<i>Product (ambient)</i>	
15 CCCC	40	5	—	55	Solid plus solution	15
DDDD	40	5	10	45	Two phases (liquid)	
66	40	5	20	35	Stable gel	
20 EEEE	40	10	—	50	Solid plus solution	20
FFFF	40	10	10	40	Solid plus solution	
GGGG	40	10	20	30	Solid plus solution	

EXAMPLE 67 TO 69

<i>Example</i>	<i>Principal surfactant</i>	<i>(a)</i>	<i>Additive (b) (i)</i>	<i>Urea</i>	<i>Water</i>	<i>Product</i>	
30 67	C ₁₄ AOS	40	Benzyl alcohol 5	—	55	Stable gel	30
68	C _{14/16} AOS	40	Benzyl alcohol 5	—	55	Stable gel	
HHHH	C ₁₄ AOS	40	Limonene 5	—	55	Lamellar phase and solution	
69	C ₁₄ AOS	40	Limonene 5	3	52	Stable gel	

EXAMPLE 71 TO 74

	<i>71</i>	<i>72</i>	<i>73</i>	<i>74</i>	
40 Sodium coconut alkyl sulphate	25	25	25	25	40
Alkyl ether sulphate	15	15	15	15	
Sodium carboxymethyl cellulose	1	—	—	1	
Formalin	—	0.75	—	0.75	
Alcalase solution	—	—	0.5	0.5	
45 Water	--- balance to 100% ---				45

EXAMPLES 75 TO 79

	<i>75</i>	<i>76</i>	<i>77</i>	<i>78</i>	<i>79</i>	
50 Sodium C _{14-C16} AOS	40	40	40	40	40	50
Dobanol 91-8	10	10	10	10	10	
Fluorescer	0.1	—	—	—	—	
55 Photobleach	—	0.006	—	—	0.006	55
Deoperfume	—	—	0.3	—	0.3	
Citric acid	—	—	—	1	1	
1,12-diperoxidodecanedioic acid (bleach)	—	—	—	5	5	
60 Water	--- balance to 100% ---					60

EXAMPLES 80 TO 82

	80	81	82	
5 Sodium coconut alkyl sulphate	40	40	40	5
Alkylbenzene sulphonate	10	10	10	
Sodium tripolyphosphate	5	—	5	
Sodium sulphite	—	5	5	
Water	--- balance to 100%---			
10				10

DISHWASHING TEST

Example	Principal surfactant (a)	Cosurfactant (b) (i)	Number of plates washed	
15				15
13	Sodium coconut alkyl sulphate	Dobanol 91-6	10	37
83	Sodium coconut alkyl sulphate	Alkylbenzene sulphonate	10	25
20 30	C ₁₄ alpha-olefin sulphonate (Na salt)	Dobanol 91-8	10	20

CLAIMS

- 25 1. An aqueous detergent composition comprising a gel wholly or predominantly in hexagonal liquid crystal form, wherein the gel comprises:
- (a) from 5 to 85% by weight of a non-ethoxylated micelle-forming non-soap surfactant having an anionic head group and an aliphatic or araliphatic hydrocarbon chain containing from 10 to 20 aliphatic carbon atoms, the anionic head group being positioned terminally or next to terminally in the hydrocarbon chain, and
- 30 (b) a second component comprising
- (b)(i) from 1 to 75% by weight of an auxiliary micelle-forming non-soap surfactant selected from:
- (b)(i)(i) anionic non-soap surfactants other than those defined under (a) above, ethoxylated nonionic surfactants having HLB values of at least 12, and amine oxides; or
- (b)(i)(ii) fatty acid mono- and diethanolamides, and ethoxylated nonionic surfactants having HLB values lower than 12;
- 35 and/or
- (b)(ii) 1 to 15% by weight of an additive which is a non-micelle-forming or weakly micelle-forming aliphatic, alicyclic, aromatic or araliphatic nonionic material having a melting point not exceeding 55°C and a dielectric constant of its liquid form of at least 2.2, selected from:
- 40 (b)(ii)(i) materials containing at least 4 carbon atoms, and containing a hydroxyl group positioned terminally or within 2 carbon atoms of the terminal position on a hydrocarbon chain or on an aromatic or alicyclic ring, and optionally one of more further polar groups; containing not more than 6 aliphatic carbon atoms if the hydroxyl group is the only polar group present or if a second polar group is present and separated from the hydroxyl group by 2 or less carbon atoms; or containing not more than 12 aliphatic carbon atoms if a second polar group is present and separated from the hydroxyl group by 3 or more carbon atoms; or
- 45 (b)(ii)(ii) materials containing at least 7 carbon atoms, and containing at least one polar group positioned terminally or within 2 carbon atoms of the terminal position on a hydrocarbon chain or on an aromatic or alicyclic ring, and/or containing ethylenic unsaturation;
- the total amount of (a) plus (b) being within the range of from 15 to 95% by weight;
- 50 and, optionally,
- (c) from 1 to 45% by weight of a second additive which is an anionic or nonionic water-soluble non-micelle-forming or weakly micelle-forming material having a polar head group and optionally an aliphatic or araliphatic hydrocarbon chain containing at most 6 aliphatic carbon atoms;
- component (c) being essential if neither an auxiliary surfactant (b)(i)(i) nor an additive (b)(ii)(i) is present; and
- 55 (d) water.
2. A composition as claimed in claim 1, wherein the surfactant (a) is a primary alkyl sulphate, a primary alkane sulphonate, an alpha-olefin sulphonate, an alkyl or alkenyl isethionate, an alpha-sulpho fatty acid salt, a fatty acid methyl ester sulphonate, or a mixture of any two or more of those.
3. A composition as claimed in claim 2, wherein the surfactant (a) comprises a primary alkyl sulphate.
- 60 4. A composition as claimed in claim 2, wherein the surfactant (a) comprises an alpha-olefin sulphonate.
5. A composition as claimed in any one of claims 1 to 4, which contains an auxiliary surfactant (b)(i), the weight ratio of surfactant (a) to surfactant (b)(i) being from 20:1 to 0.1:1.
6. A composition as claimed in claim 5, wherein the auxiliary surfactant (b)(i) is selected from alkylbenzene sulphonates, alkyl ether sulphates, ethoxylated alcohols, and alkyl phenols, fatty acid mono- and diethanolamides, and amine oxides.
- 65

7. A composition as claimed in any one of claims 1 to 4, which contains an additive (b)(ii), the weight ratio of surfactant (a) to additive (b)(ii) being from 30/1 to 3:1.
8. A composition as claimed in claim 7, wherein the additive (b)(ii) is selected from 2-phenyl ethanol, hydroxycitronellal, benzyl alcohol, linalool, thymol, terpineol, coconut fatty acid and decan-1-ol.
- 5 9. A composition as claimed in any one of claims 1 to 8, which comprises a second additive (c) which is urea. 5
10. A composition as claimed in any one of claims 1 to 9, wherein all anionic surfactants are in sodium salt form and the total level of surfactant (a) plus surfactant (b) (i) or additive (b)(ii) is from 16 to 60% by weight.
11. An aqueous detergent composition comprising a gel wholly or predominantly in hexagonal liquid crystal 10 form, wherein the gel comprises:
- (a) from 5 to 75% by weight of a non-ethoxylated micelle-forming surfactant having an anionic head group and an aliphatic or araliphatic hydrocarbon chain containing from 10 to 20 aliphatic carbon atoms, the anionic head group being positioned terminally or next to terminally in the hydrocarbon chain, and
- 15 (b) a second component comprising 15
- (b)(i) from 1 to 75% by weight of an auxiliary micelle-forming anionic, nonionic or zwitterionic surfactant other than an anionic surfactant as defined under (a), with the proviso that (b)(i) cannot be an alkylbenzene sulphonate when (a) is a fatty acid soap, or
- (b)(ii) 1 to 15% by weight of an additive which is a non-micelle-forming or weakly micelle-forming aliphatic, 20 alicyclic, aromatic or araliphatic nonionic material having a melting point not exceeding 55°C and containing at least 4 carbon atoms and at least one polar group positioned terminally or within 2 carbon atoms of the terminal position on a hydrocarbon chain or on an aromatic or alicyclic ring, 20
- the total amount of (a) plus (b) being within the range of from 15 to 85% by weight;
- (c) optionally 1 to 45% by weight of a second additive which is an anionic or nonionic water-soluble 25 non-micelle-forming material having a polar head group and optionally an aliphatic or araliphatic hydrocarbon chain containing at most 6 aliphatic carbon atoms, and 25
- (d) water.
12. A composition as claimed in claim 1, substantially as described in any one of Examples 1 to 83 herein.